The Aeronomy of Titan

D. Gautier

Departement de Recherches Spatiales (DESPA), Observatoire de Paris, F-92195 Meudon, France
E-mail: gautierd@mesioa.obspm.fr Fax: +33 1 45 07 74 69

Understanding the complex chemistry of Titan's atmosphere is a key objective of the Cassini mission and especially of the Huygens probe. Another fundamental objective is to determine the atmosphere's origin. This paper discusses the present state of our knowledge on these questions. The objectives may be reached by an interdisciplinary approach that takes advantage of the synergism possible between the various instruments aboard the Orbiter and Probe. The theoretical studies required for analysing the data are described.

1. Introduction

The set of instruments aboard the Huygens Probe and the Cassini Orbiter offers a unique opportunity for an in-depth investigation of two fundamental mission objectives: understanding the complex photochemistry occurring in Titan's atmosphere; understanding the origin of that atmosphere and, possibly, inferring the composition of Saturn's subnebula in the region where Titan formed.

2. Photochemistry of Titan's Atmosphere

The surprising complexity of Titan's atmospheric composition, initially revealed by Voyager's infrared observations, is described in a number of review papers (see, for instance, Lunine et al., 1989; Gautier, 1992; Gautier & Raulin, 1997). The hydrocarbons and nitriles detected in the stratosphere result from the dissociation of the two major components, nitrogen and methane, a process that presumably began soon after Titan's formation some 4500 million years ago. Oxygen-bearing compounds are represented by CO and CO_2. The formation of CO_2 requires the combination of CO and OH; this last species is believed to originate from the dissociation of H_2O in infalling debris. The origin of CO is more uncertain: it may also come from oxygen-bearing meteoritical material (Samuelson et al., 1983) or evaporate from a hypothetical ocean of liquid hydrocarbons (Dubouloz et al., 1989).

The main difficulty is understanding the processes leading to the formation of the detected species and then evaluating, if possible, what level of complexity Titan's chemistry may reach. This question is obviously fundamental to our consideration of exobiology (Raulin, 1997).

The vertical and horizontal distributions of nitriles and hydrocarbons in the stratosphere are far from uniform. Millimetric ground-based observations reveal that the HCN mixing ratio averaged over the disc increases with altitude (Tanguy et al., 1990). That is also the case for HC_3N (Bézard et al., 1992) and CH_3CN (Bézard et al., 1993). Previous Voyager observations provided vertical distributions of several species, but only at the North Pole (Coustenis et al., 1991). At this latitude, the mixing ratios of HCN, HC_3N, C_2H_2, C_3H_4, C_4H_2 and, possibly, C_2H_6 increase with altitude but there is no evidence that these distributions are the same everywhere on the disc. In fact, except for CO_2 and C_2H_6, which remain fairly constant (within error bars) from pole to pole, the abundances of most constituents vary with latitude. This is especially true for HCN, which shows a steady increase from south to north by as much as a factor of 30 (Coustenis & Bézard, 1995).

The case of CO is controversial. This species has been detected in Titan's near-IR spectrum by Lutz et al. (1983). Their measurements provide information on the tropospheric CO abundance but, as CO is a very stable molecule, its mixing ratio was expected to be constant ($\sim 6 \times 10^{-5}$) with height up to large altitudes. Searches for the (1-0) rotation line of this species at 115 GHz (2.6 mm) by Marten et al. (1988) with the 30 m Institut de Radio Astronomie Millimétrique (IRAM) radio telescope suggested that the stratospheric abundance probed by mm observations should be lower than the tropospheric values by at least a factor of 30. However, Gurwell & Muhleman (1995) have recently reported new microwave heterodyne observations of the (1-0) rotational transition from the stratosphere made in October 1994 with the Owens Valley Radio Observatory Millimeter Array. Their conclusion is a CO mixing ratio of $(5 \pm 1) \times 10^{-5}$ constant with height over 60-200 km, consistent with the near-IR observations of Lutz et al. (1983). CO then would be well mixed from the surface to at least 200 km in Titan's atmosphere.

This is confirmed by Hidayat et al. (1997) from IRAM and JCMT sub-mm measurements. They, however, conclude a mixing ratio of 2.5×10^{-5} below 200 km. They also suggest that CO decreases with altitude above 200 km. On the other hand, Noll et al. (1996) derived from IR measurements at 5 μm a CO mixing ratio of $1^{+1}_{-0.5} \times 10^{-5}$ in the lower atmosphere. The case of CO thus remains controversial.

No model presently provides a quantitative interpretation of these observations. Yung et al. (1984) have developed a comprehensive 1-D photochemical model of Titan's atmosphere, incorporating a large number of reactions. However, their model was unable to reproduce even the mean abundances of the species detected by Voyager in the equatorial region (Coustenis et al., 1989a). The failure stems largely from an incorrect eddy diffusion coefficient profile. Indeed, they had no information available on the vertical distributions of nitriles or hydrocarbons that could have allowed them to constrain the eddy diffusion coefficient, Kzz, as a function of the altitude. Moreover, the atmospheric scattering of solar photons was not considered and the effect of aerosols was described by an approximate transmission factor.

In order to improve the interpretation of the presently available data and to prepare for the analysis of the Cassini-Huygens observations, the following strategy has been proposed, as described in the Interdisciplinary Science proposal of the author, and is now under way.

- First, a new 1-D photochemical model has been elaborated at the University of Bordeaux (Toublanc et al., 1995). Kzz was adjusted to fit the vertical distribution of HCN inferred by Tanguy et al. (1990) from mm observations. The transfer of solar photons is described by using a Monte Carlo code designed to model the Rayleigh and Mie scattering. A number of reactions rates have been updated and the model includes 62 species involved in 249 reactions.

Toublanc et al. (1995) obtain a good fit of C_2H_2, C_2H_6 and C_3H_8 mixing ratios (Figs. 1 and 2) measured in the equatorial region by Voyager's IR imaging spectrometer (IRIS) (Coustenis et al., 1989a) as well as an acceptable fit of the CH_4 abundance (Fig. 1) observed by Voyager's UV spectrometer (UVS) (Smith et al., 1982). However, the model does not fit the C_2H_4, C_3H_4 and C_2N_2 observations; the CO_2 abundance is obtained only when CO mixing ratios consistent with IR observations, namely a few $\times 10^{-5}$, are assumed. Note that the altitudes probed vertically by IRIS are at about 130 km for C_2H_2 and C_2H_6, 125 km for C_2H_4, 110 km for C_4H_2, CO_2 and HCN, and 105 km for C_3H_8 and C_3H_4 (Coustenis et al., 1989a). In other words, there is no constraint on the stratospheric vertical distributions of these species in the equatorial region.

The interpretation of the vertical distributions observed at the North Pole requires a 3-D seasonal model taking into account the atmospheric circulation.

• Second, a General Circulation Model (GCM) has been simultaneously developed at the Laboratoire de Metéorologie Dynamique (LMD) in Paris (Hourdin et al., 1995). The zonally averaged temperatures patterns shown in Fig. 3 have been calculated at Northern Spring Equinox (lower part of the figure), which occurred a few months before Voyager l's encounter in November 1980, and at Northern Winter Solstice (upper part, 2 yr before Huygens' descent). The zonally averaged zonal winds calculated for the same epochs are plotted in Fig. 4. Hourdin et al. (1995) show that their model fits the high altitude winds pattern inferred from the thermal field measured by Voyager 1 and from measurements of Titan's 28 Sgr occultation in July 1989, 1.5 yr after the Northern Summer Solstice. In particular, the models produce a

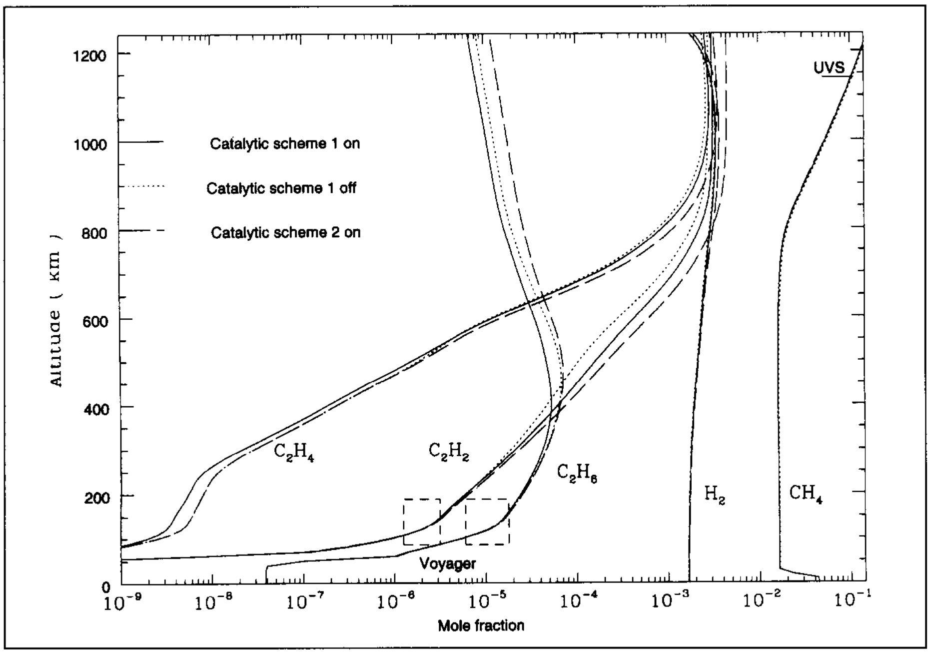


Fig. 1. Altitude profiles calculated from the photochemical model of Toublanc et al. (1995) for the mole fractions of H_2, CH_4, C_2H_2, C_2H_4 and C_2H_6. Catalytic schemes 1 and 2 refer to two different methods for the photocatalysed dissociation of CH_4 rather than direct photolysis at high altitude, as discussed by Yung et al. (1984) and Toublanc et al. (1995). Uncertainty boxes are Voyager observations in Titan's equatorial region (Coustenis et al., 1989a). From Toublanc et al. (1995).

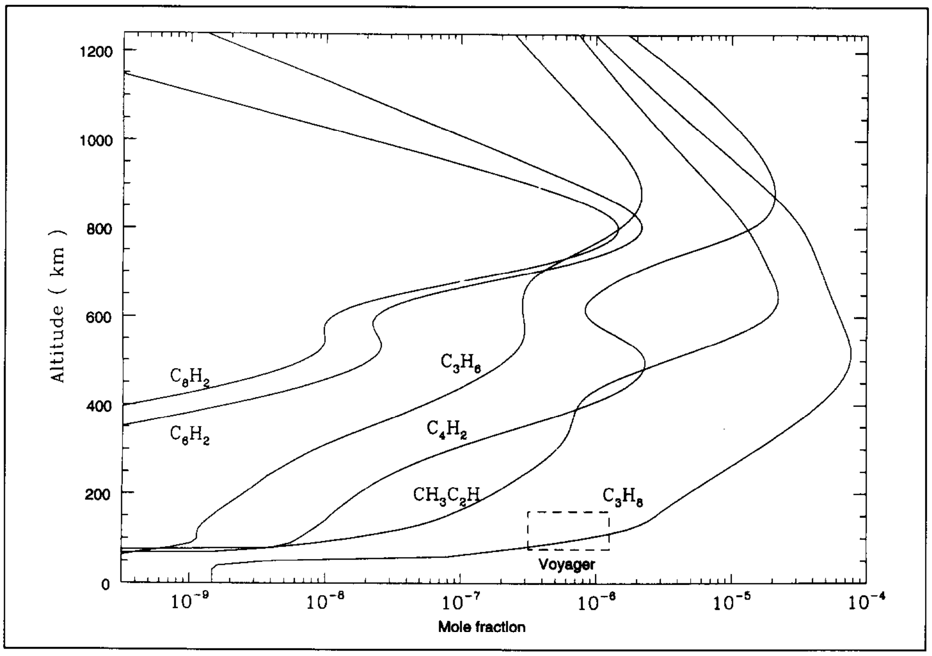
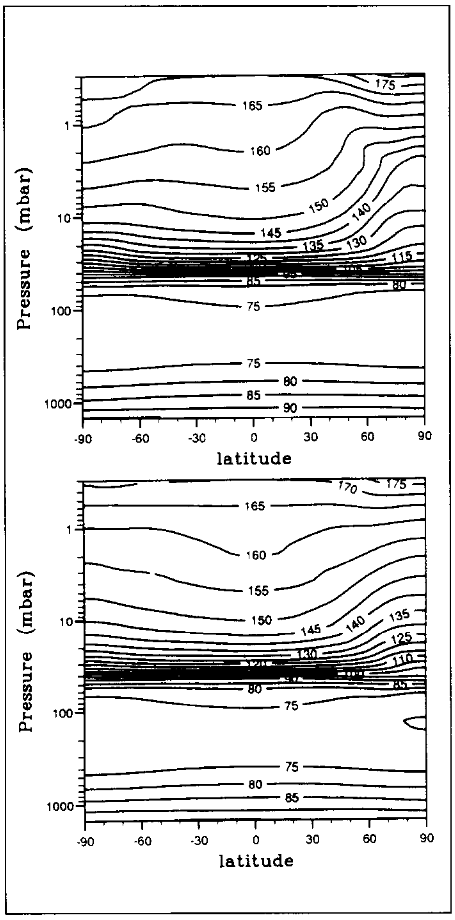
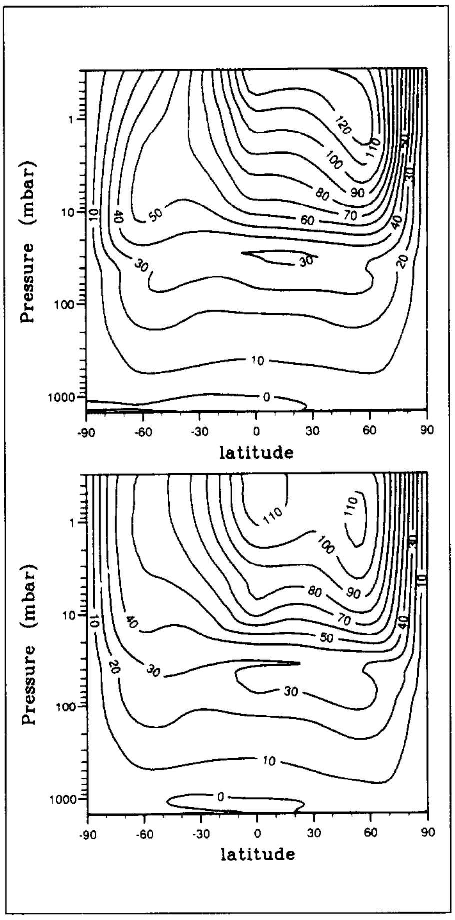


Fig. 2. As Fig. 1, but for the mole fractions of C_3H_6, C_4H_2, C_3H_8, CH_3C_2H, C_6H_2 and C_8H_2. From Toublanc et al. (1995).

Fig. 3.(left) Zonally averaged temperature (K) calculated from the General Circulation Model of Hourdin et al. (1995), at the Northern Winter Solstice (upper panel) and Northern Spring Equinox (lower panel). At the Northern Winter Solstice, the solar longitude is 270°; at the Northern Spring Equinox, it is 0°. From Hourdin et al. (1995).

Fig. 4.(right) As Fig. 3, but for zonally averaged zonal wind (m/s). From Hourdin et al. (1995).





strong superrotation of the upper atmosphere, with prograde equatorial wind velocities increasing from the surface to reach 100 m/s near the 1 mbar pressure level.

On the other hand, the model fails to reproduce the amplitude of the north-south temperature contrast. It might be that the radiative opacity, especially that due to aerosols, is incorrectly modelled. Although there is intensive theoretical study of aerosols (Cabane et al., 1993, 1997; Tomasko et al., 1997), the observational constraints, essentially derived from Voyager's remote observations, are poor. The haze IR opacity substantially contributes to the atmospheric heating and cooling (Bézard et al., 1995), but we ignore the nature, size distribution and spatial distribution of the aerosols, as well as their temporal variations. However, there is evidence for seasonal albedo variations (Lockwood et al., 1986) and for north-south brightness assymetry (Sromovsky et al., 1981) varying with time (Caldwell et al., 1992).

Both photochemical and general circulation models need to be improved (a new photochemical model was published by Lara et al., 1996). Once that is accomplished, the strategy's third step is to couple the two models and construct a 3-D model of Titan's aeronomy. Only such a model will permit us to properly analyse the expected Cassini observations.

3. Photochemistry Measurements

The suite of instruments aboard Huygens and the Orbiter has been designed to provide the data needed to understand the photochemistry of Titan, or at least to constrain a 3-D aeronomy model. Huygens' Gas Chromatograph Mass Spectrometer (GCMS) will provide the atmospheric composition at several levels in the troposphere and the stratosphere (see instrument descriptions in this volume). A complementary information set on the vertical distribution of CH_4 will come from Descent Imager/Spectral Radiometer (DISR) measurement. The Aerosol Collector & Pyrolyser (ACP), a crucial experiment for Titan's organic chemistry, will determine the chemical composition and the column abundances of aerosols, while their size, shape and vertical distributions will be obtained from DISR.

The Composite IR Spectrometer (CIRS), UV Imaging Spectrograph (UVIS) and the Radio Science Experiment will nicely complement the in situ measurements by providing the variations of composition, temperatures and aerosol optical properties across Titan's disc. The temperature profile will be retrieved from CIRS data by inversion of the far-IR spectral measurements on a large part of the disc but with a limited vertical resolution, except when horizontal viewing is possible. The radio occultation experiment will provide the thermal profile at only a few places on the disc, but with very high vertical resolution. The temperature profile inferred from CIRS at Huygens' descent location will be calibrated from Huygens Atmospheric Structure Instrument (HASI) measurements, and the radio occultation profiles subsequently compared with those of CIRS.

Once the temperature is known, vertical distributions of many stratospheric components can be retrieved from CIRS. This instrument will provide much more information than Voyager's IRIS owing to its better spectral resolution and to the fact that a large number of horizontal viewing observations is planned, compared to only one with IRIS. In addition, while IRIS had only one detector for the whole measured spectral range, CIRS has, in addition to the far-IR detectors, two mid-IR detector arrays that will greatly improve the vertical resolution of the retrieved temperature and mixing ratios profiles.

UVIS will measure the absorption due to the most important hydrocarbons and nitriles at high altitudes, and, through solar and stellar occultations, the vertical distributions of the species. The Visual and Infrared Mapping Spectrometer (VIMS) will monitor CH_4 in the troposphere.

Finally, the optical properties of aerosols and their variations with latitude will be observed by Cassini's Imaging Science Subsystems (ISS) and VIMS. CIRS is expected to detect ices exhibiting IR signatures, in addition to providing information on the spectral variation of aerosol opacity.

4. The Origin of Titan's Atmosphere

The puzzle of the composition of Titan's atmosphere is that the carbon is mainly in the form of CH_4 and the nitrogen as N_2, while thermochemical models (Lewis & Prinn, 1980) predict they should be in the form of CH_4 and NH_3, as in the giant planets, or CO (or CO_2) and N_2, as with the telluric planets.

Two scenarios of the formation of Titan's atmosphere are envisaged:

- the atmosphere might result from cometary impacts (Jones & Lewis, 1987; McKay et al., 1988; Zahnle, 1992). In such a case, its composition should reflect that of comets. We will show below that this hypothesis is not consistent with the deuterium abundance observed on Titan compared to that of Comet Halley.

- in a more conventional scenario, the atmosphere is formed by outgassing from the satellite's interior (Owen, 1982; Lunine et al., 1989). The problem then is the form of the carbon and nitrogen in the ices that constituted Titan's core 4500 million years ago.

The two scenarios can be combined. For instance, Owen & Bar-Nun (1995) advocate that contributions from both impacting comets and gases trapped in the ices accreted by the satellite must be present in the atmosphere. In this case, the respective contributions must be in a ratio that leads to a D/H ratio consistent with observations. In other words, the cometary component must be minor.

Thermochemical models of the nebula (Lewis & Prinn, 1980; Prinn & Fegley, 1989) show that, in the region of Saturn, C was mainly in the form of CO and N mainly in the form of N_2. A part of CO was also converted to heavy organics or amorphous phases but, according to Lunine (1989), probably no more than 10%. Trapped in the ices that formed Titan, N_2 could be the source of the present nitrogen atmosphere, but this scenario does not explain the large present abundance of CH_4 and the low CO/CH_4 mixing ratio.

Prinn & Fegley (1981) advocate that a subnebula was formed around Saturn as a result of the planet's initial high luminosity. Accordingly, local temperature and pressure conditions led to a conversion of CO and N_2 into CH_4 and NH_3, respectively. Note that the conversion of N_2 into NH_3 requires a very dense subnebula, which may not be realistic. Trapped in ices or in the form of clathrates, these last constituents were present in Titan's interior, as suggested by Owen (1982) and detailed in the models of Lunine & Stevenson (1987) and Grasset & Sotin (1996), and formed by outgassing the primitive atmosphere. As proposed a long time ago by Atreya (1978), NH_3 was subsequently photolysed into N_2. The high abundance of CH_4 and the very low abundance of CO are then well explained.

It is frequently mentioned in the literature that precisely determining the deuterium and argon abundances would allow us to discriminate between the various scenarios. However, the problem is complex and deserves some clarification, as discussed below.

5. Constraints

The main reservoir of deuterium in Titan's atmosphere is methane. Measuring the CH_3D/CH_4 ratio thus directly provides the D/H ratio *now*. Until recently, the D/H determinations were highly uncertain: de Bergh et al. (1986) obtained $(16.5^{+16.5}_{-8}) \times 10^{-5}$ from near-IR observations, while Coustenis et al. (1989b) deduced $(15.0^{+15.0}_{-5}) \times 10^{-5}$ from Voyager IR data. More recently, Orton (1992) derived a more precise value from high spectral measurements at 8 μm — presumably because the direct comparison of CH_3D and CH_4 lines permits a substantial improvement of the accuracy of the CH_3D/CH_4 ratio: D/H = $(7.75 \pm 2.25) \times 10^{-5}$

Moreover, some enrichment in the D/H ratio, mainly duc to the photodissociation of methane, must have occurred during Titan's history. Pinto et al. (1986) estimated the fractionation factor to be 1.7-2.2, a result confirmed by Lunine & Tittemore (1993). The low value of Orton when combined with the fractionation effect then leads to a deuterium abundance quite close to the protosolar value of $(2.6 \pm 1) \times 10^{-5}$ (Geiss, 1993) and to the revised value of $(3 \pm 0.2) \times 10^{-5}$ (Gautier & Morel, 1997). This result, if confirmed, suggests that Titan's deuterium enrichment is lower than in terrestrial ocean water as well as in meteorites, Uranus and Neptune (Lécluse et al., 1996). In any case, all D/H values measured in Titan are much lower than the recent D/H reevaluations in Comet Halley by Balsiger et al. (1995) and Eberhardt et al. (1995), who conclude it is about 31×10^{-5}. These last results imply that Titan's atmosphere did not originate mainly from cometary volatiles. Halley does not seem atypical, as similar results have been obtained in Comet Hyakutake (Bockelee-Morvan et al., 1997) and in Comet Hale-Bopp (Meier et al., 1997).

We believe that Titan's low deuterium enrichment in atmospheric methane is quite consistent with the composition model of Saturn's subnebula advocated by Prinn & Fegley (1981). The scenario for the D-enrichment is as follows:

- CH_4 and NH_3 in Saturn's subnebula initially contain only the deuterium present in the nebula's hydrogen as they are recently converted from CO and N_2. Once formed, they exchange some deuterium with HD and, as soon as the subnebula cools, they are enriched in comparison with HD (the protosolar value). H_2O coming from the nebula is not converted but may reequilibrate with HD at high temperatures in the subnebula close to Saturn. If this is the case, it will be enriched again in deuterium when the subnebula cools or when it moves outwards to the subnebula's cold regions.

- in this process, CH_4 does not equilibrate efficiently with HD at low temperatures for two reasons: (i) the isotopic exchange rate between CH_3D and HD is slower than that between H_2O and HD (Lécluse et al., 1996); (ii) the lifetime of the subnebula is much shorter than the nebula's, because its birth follows Saturn's formation (Stevenson et al., 1986). The combination of (i) and (ii) results in a lower D-enrichment in methane than, for instance, in water in the nebula. Therefore, we expect methane's D/H to be lower than in H_2O in meteorites or in water ices that presumably formed most of the cores of Uranus and Neptune.
- subsequently, water, ammonia and methane are trapped in Titan's core (Lunine & Stevenson, 1987; Grasset, 1994; Grasset & Sotin, 1996), although the satellite's relatively low density suggests that water might be somewhat deficient (Stevenson, 1985; Lunine, 1989). The primitive atmosphere is then formed by outgassing these volatiles from the interior. NH_3 is converted into N_2 as previously mentioned and H_2O condenses; CH_4 then becomes the main deuterium reservoir in Titan's atmosphere. Assuming a subnebula D-enrichment in methane of 1.4 times the protosolar value (Lunine & Tittemore, 1993), and a subsequent photochemical enrichment by a factor of 2.2, the D/H ratio in methane now is 8×10^{-5}, in remarkable agreement with Orton's value of 7.75×10^{-5}.

This scenario assumes the validity of the thermochemical model of Prinn & Fegley (1981), which is based on a questionable model of Saturn's subnebula. However, although the temperature-density conditions are different, it is encouraging to observe that the conversion of CO and N_2 in CH_4 and NH_3, respectively, occurs, as predicted by the theory, in the tropospheres of Jupiter, Saturn and Uranus. The unexpected detection of CO and HCN in Neptune's upper troposphere (Marten et al., 1993) could suggest a failure of the model, but Lodders & Fegley (1994) have proposed an attractive explanation for the presence of CO. HCN could be formed from the dissociation by cosmic rays of N_2 coming from the planet's interior; in that case, the N_2 abundance would be much higher than predicted by the thermochemical calculations. However, HCN may also be produced by nitrogen atoms escaping from Triton and thus its observed abundance does not necessarily require an internal origin for all nitrogen (Lellouch et al., 1994). At present there is only a presumption, based mainly on the interpretation of Neptune's cm spectrum (Gautier et al., 1995), for the level of N_2 in Neptune's upper troposphere being higher than predicted by thermochemical models.

We can conclude from this exercise that a precise determination of the D/H ratio in Titan's atmosphere by Huygens should provide firm constraints on the chemical composition of Saturn's subnebula. A low D/H ratio would confirm the scenario of Prinn & Fegley (1981). A high value, say of the order of that in Uranus and Neptune, would imply a nebula origin for the ices that formed Titan. A value compatible with the 300 ppm derived for Comet Halley (Balsiger et al., 1994; Eberhardt et al., 1995) — inconsistent with the current data for both Titan and the giant planets — would imply that the atmosphere was formed from cometary impacts.

It is desirable to model the spatio-temporal evolution of methane's deuterium enrichment in Saturn's subnebula. Measurements of the coefficient of isotopic exchange betwen CH_3D and HD were recently made for the first time in the laboratory (Lécluse et al., 1995). These data, together with improved models of Saturn's subnebula, will permit a more precise calculation of the kinetics of the isotopic exchange between methane and hydrogen in the subnebula as a function of time and of the distance to Saturn. This work, undertaken by the author in collaboration with Francois Robert (Museum d'Histoire Naturelle, Paris) and Berangère Dubrulle (CEA, Saclay), is in progress.

6. Titan's Argon Abundance

The history of the successive estimates of Titan's argon abundance illustrates the difficulty in remotely detecting noble gases. The hypothesis of there being a substantial amount of argon in Titan's atmosphere originates from an erroneous estimate of the lower limit of the mean molecular weight by Samuelson et al. (1981), who advocated that the atmosphere is fairly transparent at 540 cm^{-1}, thus permitting a kind of calibration of the brightness temperature at this frequency by comparison with the surface temperature derived from radio occultation measurements. A molecular weight higher than 28 implies a gaseous constituent heavier than nitrogen. Argon is the most likely candidate as it would not condense under Titan's atmospheric conditions. However, as pointed out by Owen (1982), only a tiny amount of ^{40}Ar, which comes from the disintegration of ^{40}K, can be present in the atmosphere. The assumption that atmospheric argon is substantially abundant implies that it is in the form of primordial isotopes ^{36}Ar and ^{38}Ar, initially present in the solar nebula or in Saturn's subnebula, and trapped in ices. Subsequently, Toon et al. (1988) advocated that the atmosphere is not transparent at 540 cm^{-1}. Lellouch et al. (1989) reanalysed the comparison of the radio occultation data with the IRIS measurements and concluded that only an upper limit of 21% for the argon mole fraction could be inferred. Subsequently, Strobel et al. (1992) derived an upper limit of 14%, which was then revised down to 10% at 3σ (Strobel et al., 1993). More recently, Courtin et al. (1995) modelled Titan's far-IR spectrum over 200-600 cm^{-1}, including the fine structure of the H_2-H_2, H_2-CH_4 and H_2-Ar dimers around 355 cm^{-1} and 585 cm^{-1}. The comparison with Voyager data leads these authors to infer an upper limit of 6% at 3σ for the Ar mole fraction.

This low argon abundance does not conflict with the scenario mentioned above for Titan's formation. Lunine et al. (1989) show that it would be consistent with the derivation of N_2 from NH_3. Unfortunately, the test might not be decisive, as Owen and Bar-Nun (1995) recently pointed out the difficulty of incorporating Ar in ices at temperatures expected in Saturn's subnebula. As a consequence, a CO-N_2 subnebula would not lead to a high argon abundance either. These authors predict that Titan's Ar mole fraction will not exceed 1%. However, the measurement of the $^{36}Ar/^{40}Ar$ ratio should constrain the formation models. A substantial abundance of ^{40}Ar would imply strong tectonic activity on Titan.

7. Atmospheric Origin Measurements

The key instrument is definitely Huygens' mass spectrometer, which will provide the abundances of deuterium and argon's isotopes. However, the importance of these determinations makes complementary or redundant information necessary. This will come from the determination by CIRS of the CH_3D/CH_4 ratio at 8 μm. The highest spectral resolution of CIRS compared to that of Voyager's IRIS will also provide a better analysis of the H_2 dimer features and then permit detection of the H_2-Ar Van der Waals molecule or an upper limit on argon's abundance. A substantial amount of argon would affect the mean molecular weight, which can be derived by two different methods. One was used for Voyager, namely combining radio occultation profiles and IR spectra. The second approach is to derive the molecular weight, through the equation of state, from temperature and pressure measured by HASI.

8. Final Remarks

The payload aboard Huygens and the Orbiter has been carefully designed to obtain answers to fundamental questions concerning the aeronomy and origin of Titan's atmosphere. We have shown in this paper that the prospect of these results has initiated or stimulated a number of observational and theoretical works that enhance the mission's value even further. Expected spectroscopic observations of Titan from ESA's Infrared Space Observatory are highly promising. We hope to detect new species in the atmosphere or improve our knowledge of their vertical distributions. The Hubble

Space Telescope will help us to constrain aerosol models. Considerable theoretical work must be done in poorly known domains, such as the physico-chemistry of Saturn's subnebula and the formation and the evolution of Titan's core.

References

Atreya, S. K., Donahue, T. M. & Kuhn, W. R. (1978). Evolution of a nitrogen atmosphere on Titan. *Science* **201**, 601-613.

Balsiger, H., Alwegg, K. & Geiss, J. (1995). D/H and $^{18}O/^{16}O$-ratio in the hydronium ion and in neutral water from in situ ion measurement in comet Halley. *J. Geophys. Res.* **A4**, 5827-5834.

Bézard, B., Marten, A. & Paubert, G. (1992). First Ground-based Detection of Cyanoacetylene on Titan. *Bull. Am. Astron. Soc.* **24**, 953.

Bézard, B., Marten, A. & Paubert, G. (1993). Detection of Acetonytrile on Titan. *Bull. Am. Astron. Soc.* **25**, 1100.

Bézard, B., Coustenis, A. & McKay, C. P. (1995). Titan's stratospheric temperature asymetry: a radiative origin? *Icarus* **113**, 267-276.

Bockelee-Morvan, D., Gautier, D., Lis, D. C., Young, K., Keene, J., Phillips, T., Owen, T., Crovisier, J., Golsmith, P. F., Bergin, E. A., Despois, D. & Wooten, A. (1997). Deuterated Water in Comet C/1996 B2 (Hyakutake) and its implications for the structure of the Primitive Solar Nebula. *Icarus* (Submitted).

Cabane, M., Rannou, P., Chassefière, E. & Israel, G. (1993). Fractal aggregates in Titan's atmosphere. *Planet. Space Sci.* **41**, 257-267.

Cabane, M., Chassefière, E. & Israel, G. (1997). Microphysical Models of Titan's Aerosols. In *Huygens: Science, Payload and Mission*, ESA SP-1177.

Caldwell, J., Cunningham, C. C., Antony, D., White, H. P., Groth, E. J., Hasan, H., Noll, K., Smith, P. H., Tomasko, M. G. & Waver, H. A. (1992). Titan: Evidence for seasonal change: A comparison of Hubble Space Telescope and Voyager images. *Icarus* **96**, 1-9.

Courtin, R., Gautier, D. & McKay, C. P. (1995). Titan's Thermal Emission Spectrum: Reanalysis of the Voyager Infrared Measurements. *Icarus* **114**, 144-162.

Coustenis, A. & Bézard, B. (1995). Titan's Atmosphere from Voyager infrared observations. IV. Latitudinal variations of temperature and composition. *Icarus* **113**, 267-276.

Coustenis, A., Bézard, B. & Gautier, D. (1989a). Titan's Atmosphere from Voyager Infrared Observations. I. The gas composition of Titan's equatorial region. *Icarus* **80**, 54-76.

Coustenis, A., Bézard, B. & Gautier, D. (1989b). Titan's Atmosphere from Voyager Infrared Observations. II. The CH_3D abundance and D/H ratio from the 900-1200 cm^{-1} spectral region. *Icarus* **82**, 67-80.

Coustenis, A., Bézard, B., Gautier, D., Marten, A. & Samuelson, R. (1991). Titan's Atmosphere from Voyager Infrared Observations. II. Vertical distributions of hydrocarbons and nitriles near Titan's north pole. *Icarus* **89**, 152-167.

De Bergh, C., Lutz, B., Owen, T. & Chauville, J. (1986). Monodeuterated methane in the outer solar system. III. Its abundance on Titan. *Astrophys. J.* **311**, 501-510.

Dubouloz, N., Raulin, F., Lellouch, E. & Gautier, D. (1989). Titan's hypothesized Ocean properties: the influence of surface temperature and atmospheric composition uncertainties. *Icarus* **82**, 81-96.

Eberhardt, P., Reber, M., Krankowsky, D. & Hodges, R. (1995). The D/H and $^{18}O/^{16}O$ ratios in water from comet P/Halley. *Astron. Astrophys.* **302**, 301-316.

Gautier, D. (1992). The composition of the Titan atmosphere. In *Proceedings Symposium on Titan*, ESA SP-338, ESA Publications Division, ESTEC, Noordwijk, The Netherlands, pp43-52.

Gautier, D. & Morel, P. (1997). A reestimate of the protosolar D/H ratio from $^3He/^4He$ solar wind measurements. *Astron. Astrophys.* **323**, L9-L12.

Gautier, D., Conrath, B. J., Owen, T., de Pater, I. & Atreya, S. K. (1995). The Troposphere of Neptune. In *Neptune and Triton* (Ed. D. P. Cruikshank), The University of Arizona Press, pp547-611.

Grasset, O. (1994). Structure et Dynamique interne de Titan: études théoriques et expérimentales. Thése, Université de Paris-XI, Orsay, 12 December.

Grasset, O. & Sotin, C. (1996). The Cooling Rate of a Liquid Shell in Titan's Interior. *Icarus* **123**, 101-112.

Gurwell, M. A. & Muhleman, D. O. (1995). CO on Titan: Evidence for a Well-Mixed Atmosphere. *Icarus* **117**, 375-382.

Hidayat, T., Marten, A., Bézard, B., Gautier, D., Owen, T., Matthews, H. E. & Paubert, G. (1997). Millimeter and Submillimeter Heterodyne Observations of Titan: The Vertical Profile of Carbon Monoxide on its Stratosphere. *Icarus* (Submitted).

Hourdin, F., Talagrand, O., Sadourny, R., Courtin, R., Gautier, D. & McKay, C. (1995). Numerical Simulation of the General Circulation of the atmosphere of Titan. *Icarus* **117**, 358-374.

Jones, T. D. & Lewis, J. S. (1987). Estimated impact shock production of N_2 and organic compounds on early Titan. *Icarus* **72**, 381-393.

Lara, L. M., Lellouch, E., Lopez-Moreno & Rodrigo, R. (1996). Vertical distribution of Titan's atmospheric neutral constituents. *JGR* **101**, 26361-26283.

Lécluse, C., Robert, F., Gautier, D. & Guiraud, M. (1996). Deuterium enrichment in giant planets. *Planet. Space Sci.* **44**, 1579-1592.

Lellouch, E., Coustenis, A., Gautier, D., Raulin, F., Dubouloz, N. & Frère, C. (1989). Titan's Atmosphere and Hypothesized Ocean: A reanalysis of the Voyager 1 Radio-Occultation and IRIS 7.7 μm Data. *Icarus* **79**, 328-349.

Lellouch, E., Romani, P. N. & Rosenqvist, J. (1994). The Vertical Distribution and Origin of HCN in Neptune's Atmosphere. *Icarus* **108**, 112-136.

Lewis, J. S. & Prinn, R. G. (1980). Kinetic inhibition of CO and N_2 reduction in the solar nebula. *Astrophys. J.* **238**, 357-364.

Lockwood, G. B., Lutz, B. L., Thompson, D. T. & Bus, E. S. (1986). The albedo of Titan. *Astrophys. J.* **303**, 511-520.

Lodders, K. & Fegley, B. Jr. (1994). The Origin of Carbon Monoxide in Neptune's Atmosphere. *Icarus* **112**, 368-375.

Lunine, J. (1989). The Urey Prize Lecture: Volatile Processes in the Outer Solar System. *Icarus* **81**, 1-13.

Lunine, J., Atreya, S. K. & Pollack, J. B. (1989). Present state and chemical evolution of the atmospheres of Titan, Triton, and Pluto. In *Origin and Evolution of Planetary and Satellite Atmospheres* (Eds. S. K. Atreya, J. B. Pollack & M. S. Matthews), University of Arizona Press, Tucson, Arizona, USA, pp605-665.

Lunine, J. & Stevenson, D. J. (1987). Clathrate and Ammonia Hydrates at High Pressure: Application to the Origin of Methane on Titan. *Icarus* **70**, 61-77.

Lunine, J. I. & Tittemore, W. C. (1993). Origins of Outer-Planet Satellites. In *Protostars and Planets III* (Eds. E. H. Levy & J. I. Lunine), Univ. of Arizona Press, Tucson, Arizona, USA, pp1149-1176.

Lutz, B. L., De Bergh, C. & Owen, T. (1983). Titan: Discovery of carbon monoxide in its atmosphere. *Science* **220**, 1374-1375.

Marten, A., Gautier, D., Tanguy, L., Lecacheux, A., Rosolen, C. & Paubert, G. (1988). Abundance of Carbon Monoxide in the Stratosphere of Titan from Millimeter Heterodyne Observations. *Icarus* **76**, 558-562.

Marten, A., Gautier, D., Owen, T., Sanders, D. B., Matthews, H. E., Atreya, S. K., Tilanus, R. P. J. & Deane, J. R. (1993). First observations of CO and HCN on Neptune and Uranus at millimeter wavelenghts and their implications for atmospheric chemistry. *Astrophys. J.* **406**, 285-297.

McKay, C. P., Scatterwood, T. W., Pollack, J. B., Borucki, W. J. & Van Ghysegham, H. T. (1988). High temperature shock formation of N_2 and organics on primordial Titan. *Nature* **332**, 520-522.

Meier, R., Owen, T. C., Matthews, H. E., Jewitt, D. C., Bockelee-Morvan, D., Crovisier, D. & Gautier, D. (1997). Deuterium in Comet C/1995 O1 (Hale-Bopp): a Determination of HDO/H_2O. *Science* (Submitted).

Noll, K. S., Gerballe, T. S., Knacke & Pendleton, Y. J. (1996). Titan's 5 μm spectral window: carbon monoxide and the albedo of the surface. *Icarus* **124**, 625-631.

Owen, T. (1982). The composition and origin of Titan's atmosphere. *Planet. Space Sci.* **30**, 833-838.

Owen, T. & Bar-Nun, A. (1995). Comets, Impacts, and Atmospheres. *Icarus* **116**, 215-226.

Orton, G. (1992). Ground-Based observations of Titan's Thermal Structure. In *Proceedings Symposium on Titan*, ESA SP-338, ESA Publications Division, ESTEC, Noordwijk, The Netherlands, pp81-88.

Pinto, J.-P., Lunine, J. I., Kim, S. I. & Yung, Y. L. (1986). D to H ratio and the origin and evolution of Titan's atmosphere. *Nature* **319**, 388-390.

Prinn, R. G. & Fegley, B. (1981). Kinetic inhibition of CO and N_2 reduction in circumplanetary nebulae: implications for satellite composition. *Astrophys. J.* **249**, 308-317.

Prinn, R. G. & Fegley, B., Jr. (1989). Solar Nebula Chemistry: Origin of Planetary Satellite and Cometary Volatiles. In *Origin and Evolution of Planetary and Satellite Atmospheres* (Eds. S. K. Atreya, J. B. Pollack & M. S. Matthews), The University of Arizona Press, Tucson, Arizona, USA, pp78-136.

Raulin, F. (1997). Titan's organic chemistry and exobiology. In *Huygens: Science, Payload and Mission,* ESA SP-1177.

Samuelson, R. E., Hanel, R. A., Kunde, V. G. & Maguire, W. C. (1981). Mean molecular weight and hydrogen abundance of Titan's atmosphere. *Nature* **292**, 688-693.

Samuelson, R. E., Maguire, W. C., Hanel, R. A., Kunde, V. G., Jennings, D. E., Yung, Y. L. & Aikin, A. C. (1983). CO_2 on Titan. *J. Geophys. Res.* **88**, (A11), 8709-8715.

Sromovsky, L. A., Suomi, V. E., Pollack, J. B., Krauss, R. J., Limaye, S. S., Owen, T., Revercomb, H. E. & Sagan, C. (1981). Implications of Titan's north-south brightness asymmetry. *Nature* **292**, 698-702.

Stevenson, D. J. (1985). Cosmochemistry and structure of giant planets and their satellites. *Icarus* **62**, 4-15.

Stevenson, D. J., Harris, A. W. & Lunine, J. I. (1986). Origins of satellites. In *Satellites* (Eds. A. J. Burns & M.S. Matthews), Univ. of Arizona Press, Tucson, Arizona, USA, pp39-88.

Strobel, D. F., Summers, M. E. & Zhu, X. (1992). Titan's upper atmosphere: Structure and ultraviolet emissions. *Icarus* **100**, 512-526.

Strobel, D. F., Hall, D. T., Zhu, X. & Summers, E. (1993). Upper limit on Titan's atmospheric argon abundance. *Icarus* **103**, 333-336.

Tanguy, L., Bézard, B., Marten, A., Gautier, D., Gerard, E., Paubert, P. & Lecacheux, A. (1990). Stratospheric profile of HCN on Titan from millimeter observations. *Icarus* **85**, 43-57.

Tomasko, M. G., Lemmon, M., Doose, L. R., Smith, P. H., Eibl, A. & West, R. A. (1997). Models of the penetration of Sunlight into the Atmosphere of Titan. In *Huygens: Science, Payload and Mission*, ESA SP-1177.

Toon, O. B., McKay, C. P., Courtin, R. & Ackerman, T. P. (1988). Methane rain on Titan. *Icarus* **75**, 255-284.

Toublanc, D., Parisot, J.-P., Brillet, J., Gautier, D., Raulin, F. & McKay, C. P. (1995). Photochemical Modeling of Titan's Atmosphere. *Icarus* **113**, 2-26.

Yung, Y. L., Allen, M & Pinto, J. P. (1984). Photochemistry of the atmosphere of Titan: Comparison between model and observations. *Astrophys. J. Suppl.* **55**, 465-506.

Zahnle, Z. (1992). Impact Origin of Titan's Atmosphere. In *Proceedings Symposium on Titan*, ESA SP-338, ESA Publications Division, ESTEC, Noordwijk, The Netherlands, pp19-28.